



## PATENT SPECIFICATION

DRAWINGS ATTACHED

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## COMPLETE SPECIFICATION

## Improvements in or relating to Metalliferous Compositions

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improving, particularly at elevated temperatures, the modulus, tensile strength, fatigue strength, hardness, creep resistance and crack-propagation resistance of metals having melting points in the range of 50 to 720° C, and improving the tensile strength, yield strength, hardness, stress-rupture, and creep resistance of metals having melting points above 720° C. The improvement is accomplished by incorporating very small, dispersed particles of a refractory metal oxide into a mixture of an inactive metal with an active metal which bonds the inactive metal to the dispersed particles. For metal mixtures having a melting point above 720° C, the refractory metal oxide particles are incorporated into the inactive metal and the dispersion so obtained is mixed with a molten active metal and the mixture is cast.

In prior efforts to produce metals having modified properties, particularly improved stress rupture, high temperature tensile and yield strength, and creep resistance it was thought that care should be used to exclude oxide occlusions. Expensive procedures have been employed for purging oxygen and oxygen compounds from molten masses of metal. More recently, in the manufacture of cermets, processes have been worked out in which, by powdered metal techniques, certain metals containing oxide coatings can be shaped as a sintered mass and upon cooling, heterogeneous masses can be obtained. In

such cermets, the metal oxide is present as particles which, in general, are substantially larger than 1 micron in size. While cermets have found valuable applications in industry, the necessity of forming them by sintering rather than by molten metal procedures renders their cost so great that they can be used only in specialty applications.

It has not hitherto been believed possible, by molten metal procedures, to produce satisfactory high-melting metals containing dispersions of refractory materials. Neither has it been known how to bond finely divided oxides to metals nor how to disperse them in metals. Combinations of aluminium oxide and sintered aluminium metal, although useful over a wider temperature range than aluminium metal, suffer from the disadvantage that the aluminium oxide is not adequately bonded to the aluminium metal. If one heats such a mixture to a temperature above the melting point of aluminium metal, a separation occurs into the two component parts, alumina and aluminium metal. This creates special problems, particularly in such processes as casting and welding.

Moreover, with higher-melting metals, if one merely adds a finely divided refractory metal oxide to a molten mass of such metal, the oxide sinters and coalesces to a slag of aggregated particles which cannot be re-dispersed.

In the conventional cermets of the prior art relatively large oxide refractory bodies are used. Because of this, or because bonding of the refractory to the metal has not been achieved, such products suffer from low tensile strength and brittleness; that is, the impact strength is strictly limited. The ductility of the parent metal is completely lost.

We have now found that if the refractory oxide is properly selected with reference to its free energy of formation, is in the form

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of substantially discrete particles of a limited size range, has a ratio of surface area to density within a specific, relatively narrow range, and is embedded in an inactive metal, if also there is present in the molten metal to which it is added a suitable proportion of an active metal, then dispersions of refractory metal oxides are not detrimental in metals as above-described, even when the dispersions are prepared by molten metal technology, but, on the contrary, the metal products having a melting point of 50 to 720° C so produced have remarkably improved properties with respect to high-temperature tensile and fatigue strength, modulus, high-temperature stress rupture, hardness and crack-propagation resistance, and the metal products with melting points above 720° C are remarkably improved with respect to such properties as high-temperature tensile and yield strength, high-temperature stress rupture, hardness, and creep resistance. Surprisingly, when refractories as described are introduced into certain molten baths the viscosity of the bath is substantially increased, so that the molten metal can be handled in a highly unorthodox manner. It can be spun into fibres, handled like putty, and even molded into formed bodies at temperatures considerably above the melting point of the metal. The utility of these remarkable changes in the properties of the metal will be readily apparent to those skilled in the art.

More particularly the invention provides metalliferous compositions having a melting point of from 50 to 720° C, said compositions comprising a dispersion, in a mixture of (a) a metal having a melting point above 50° C, and having an oxide reducible by hydrogen below 1000° C, with (b) an active metal having an oxide irreducible by hydrogen below 1000° C, of (c) substantially discrete submicron-sized particles, preferably having an average dimension of 5 to 500 millimicrons, and a surface area, in square meters per gram, of  $12/D$  to  $1200/D$  where  $D$  is the density of the particles in grams per milliliter, of a refractory metal oxide which is insoluble in said metal mixture, is thermally stable to at least 500° C, and has a melting point above 1000° C and a free energy of formation ( $\Delta F$ ) at 1000° C above 60 kilocalories per gram atom of oxygen (kcal./gm.at.O) and above the  $\Delta F$  of the oxide of the active metal, the proportion of active metal being at least the minimum which prevents drossing out of the refractory oxide particles when the composition is maintained in a quiescent molten state for  $\frac{1}{2}$  hour.

The invention also provides cast compositions as just described which have a melting point above 720° C and in which (1) the metal (a) is one with an oxide having a free

energy of formation at 27° C below 88 kcal. atom of oxygen, (2) the refractory particles have an average dimension of 5 to 1000 millimicrons and a surface area of  $6/D$  to  $1200/D$ , and are thermally stable at the melting point of the composition and have a melting point above that of the composition, and have a  $\Delta F$  at 1000° C above 90 kcal. per gram atom of oxygen, and (3) the proportion of active metal is at least 4 mol per cent, based upon the refractory particles.

The invention further provides processes for producing the lower-melting novel compositions comprising the step of mixing the refractory oxide particles with a molten mass of metal (a), at a temperature between the melting point of the metal mass and 720° C, there being present in the mixture at least the minimum proportion of active metal (b) which prevents drossing out of the refractory oxide particles when the mixture is maintained in a quiescent state for  $\frac{1}{2}$  hour, the intensity of mixing being sufficient to effect dispersion of the oxide particles to a substantially discrete state in the mixture. Preferably the refractory metal oxide is added to the molten metallic mass in contact with from  $7.5 \times 10^{-4}A$  to  $7.5 \times 10^{-2}A$  grams of oxygen per gram of the refractory metal oxide,  $A$  being the surface area of said refractory metal oxide in square meters per gram.

The invention also includes a process for producing the higher-melting composition, which process comprises the step of (1) mixing a dispersion of the refractory oxide particles in an inactive metal with a molten mass of metal, there being present in the mixture at least 4 mol per cent of active metal based upon the refractory oxide and the intensity of mixing being sufficient to maintain dispersion of the refractory oxide particles in a substantially discrete state, and (2) casting the molten mixture. In preferred compositions the refractory oxide has a free energy of formation greater than 105 kcal. per gram atom of oxygen. Higher-melting point compositions in which the active metal has a melting-point above 1200° C are particularly preferred, more particularly, compositions in which the active metal is titanium present in a proportion of at least 50% by weight.

The invention is still further directed to low-melting compositions comprising the refractory oxide particles dispersed in active metal (b), which compositions are suitable for further mixing with inactive metal (a).

According to this aspect of the invention we provide a cast, metalliferous composition having a melting point in the range of 50 to 720° C said composition comprising an active metal having an oxide which is irreducible by hydrogen below 1000° C and has a free energy of formation at 27° C above

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88 Kcal. per gram of oxygen, said metal having dispersed therein up to 80 per cent by volume of refractory oxide having a melting point above  $1000^{\circ}\text{C}$ , and a free energy of formation at  $1000^{\circ}\text{C}$  above 60, the refractory oxide being in the form of substantially discrete particles having an average dimension of 5 to 500 millimicrons and a surface area, in square meters per gram, of  $12/D$  to  $1200/D$  where  $D$  is the density of the particles in grams per milliliter. Preferably the active metal is magnesium, aluminium, zinc, lithium, sodium, potassium, rubidium, cesium calcium, barium or strontium or an alloy of two or more of these metals.

In the drawings, Figure 1 is a fanciful representation of a low-melting product in which there is refractory oxide particle, silica, having a surface bonded to an active metal, calcium, the surface being metallophilic by reason of the combination therewith of calcium atoms, and

Figure 2 is a cross section of a mass of mixed active and inactive metals containing dispersed therein a refractory oxide filler, and

Figure 3 is a similar cross section in which the refractory oxide is in the form of fibre particles, and

Figure 4 is a representation similar to that of Figure 1, but of a high-melting product in which there is a refractory oxide, thoria, having a surface bonded to an active metal, titanium.

In the description which follows, the invention will be described, with respect to particular embodiments thereof, by way of example only.

Referring again to the drawings, in Figure 1, line 1—1 represents the surface of a silica particle containing surface silanol

(—SiOH) groups. When this surface is heated, condensation between silanol groups occurs with the formation of siloxane linkages on the surface as shown at line 2—2 of Figure 1. If, while maintaining the temperature at about  $600^{\circ}\text{C}$ , this surface is subjected to contact with calcium metal vapour under non-oxidizing conditions, there is obtained a particle having a core of silica and a surface of calcium silicide (CaSi) and calcium silicate (CaOSi) groups. The specific surface area, which was initially in the range of 5.6 to 560, is not changed substantially. When the so-treated silica powder is added to and mixed with a molten mass of an inactive metal such as lead, together with additional calcium metal, and the molten mass is solidified, the metal obtained has substantially increased strength and this increase is evident even at elevated temperatures—specifically at temperatures just below

the melting point of the metal.

In Figure 2 is dispersion of a refractory oxide in a solidified mixture of active and inactive metals is shown. Particles 4 are the refractory oxide which are distributed substantially uniformly through the mass of metal 5. It is, of course, not possible to see in such a representation the manner in which the oxide particles are bonded to the metal; however, wetting of the particles by the metal can be inferred from observation of the manner in which the refractory readily becomes dispersed and stays dispersed in the metal when the refractory is added to the molten metal. On the other hand, refractories which are not wetted by the molten metal float on top or, in other words, make manifest the fact that they are metallophobic.

In Figure 3 there is shown another embodiment in which the refractory 7 in the metal 6 is in the form of elongated particles such as fibers, extremely increasing the viscosity of the molten metal at low volume loadings. Thus, if it is important in a particular application to keep down the total amount of refractory added, one can use an anisotropic refractory body.

In Figure 4, the line 1—1 represents the surface of a thoria particle containing sur-

face —Th—OH groups. When this surface is heated, condensation between the

—Th—OH groups occurs with the formation

of oxide linkages as shown at line 9—9. If, while maintaining the temperature at about  $720^{\circ}\text{C}$ , this surface is subjected to contact with titanium metal under non-oxidizing conditions, there is obtained a particle having a core of thoria and a surface of titanium-thorium groups. The specific surface area, which was initially in the range of 0.6 to 120, is not changed substantially. When thoria-molybdenum powder is added to and mixed with a molten mass of an active metal containing titanium, the above reactions occur, and when the molten mass is solidified, the metal obtained has substantially increased strength. This increase is especially evident at elevated temperatures—specifically at temperatures only somewhat below the melting point of the metal.

#### *The Refractory Oxide.*

In describing this invention the dispersed refractory particles will sometimes be referred to as "the filler." The word "filler" is not used to mean an inert extender or diluent; rather, it means an essential constituent of the novel compositions which contributes new and unexpected properties to the metalliferous product. Hence, the filler is an active ingredient.

The refractory which is dispersed in a molten metal mixture in accordance with the present invention must have certain characteristics to give the desired effects. It must be a refractory—that is, it must not melt in the molten metal to which it is added—and in general, should have a melting point above 1000° C. It should not sinter or lose its size or shape, and it should not be soluble to any substantial degree in the metal to which it is to be added. The art is familiar with refractories generally, and one skilled in the art will have no trouble recognizing a refractory answering the above description.

One advantage of the present invention over the prior art is that hard particles of a controlled size and shape can be added to metals to reinforce their properties. If the hard particles are soluble in the metal, then recrystallization and particle growth will occur, particularly when the metal is molten. The result is that the size of the hard particles will be increased and the advantages of small particles will be lost. Filler particles which are soluble to an extent less than 0.1%, at 1000° C by weight are required. Preferred are particles which are less soluble than 0.001%.

The refractory oxide filler must be thermally stable in the molten metal to which they are added. By "thermally stable" is meant that the filler does not melt or decompose below the indicated temperatures. The refractory may have a surface coating which does not answer this description, as in the case of the calcium silicide of Figure 1, but if so, the coating must be sufficiently thin that the refractory nature of the particles is not lost.

The ultimate particles in the filler must be in the submicron range and preferably have an average dimension in the range of 5 to 500 millimicrons. Because here is a considerable difference of density in various refractories, the size of the refractory particles is aptly defined in the terms of their density and surface area per unit weight—that is, specific surface area. This also obviates the difficulties encountered when isotropic particles are involved. Specific surface area is, of course, expressed in square meters per gram ( $\text{m}^2/\text{g}$ ). The refractory particles used according to the present invention should have a specific surface area in the range of  $6/D$  to  $1200/D$   $\text{m}^2/\text{g}$ , where  $D$  is the density of the particles in grams per milliliter ( $\text{g}/\text{ml}$ ). In the case of spheroids, this corresponds to particles having a diameter of from 5 to 1000 millimicrons. Below 5 millimicrons, it is difficult to obtain dispersions of the particles in metals because of a tendency to sintering. Above 1000 millimicrons the effect of the finely divided refractory oxide in the metal is to produce brittleness, and development of the desired

physical properties of the final metal mixture will not be achieved. Particles having a surface area in the range of  $600/D$  to  $24/D$   $\text{m}^2/\text{g}$  are especially preferred.

The surface area of any material can readily be determined from nitrogen adsorption data by the well-known method of Brunauer, Emmett and Teller, which is described in "Symposium on New Methods for Particle Size Determination in the Sub-sieve Range" (Philadelphia: American Society for Testing Materials, 1941 page 95).

The finely divided refractory can be in the form of either crystalline or amorphous particles. The particles can be spherical, particularly in the case of amorphous materials, or they can have specific crystalline shapes—for example, cubes, fibers, platelets, and other shapes. In the case of fibers and plate-like materials, unusual and beneficial results can be obtained due to the shape factor of the particles. For instance, fibers and platelets cause the molten metals to become very highly viscous at considerably lower volume loadings than are necessary with spheroids or cubes. On the other hand, to lower the density of a low-melting metal like lead, one uses a high volume loading of a low density filler such as spherical silica particles, while for a high-melting metal such as tungsten one uses a high volume of a low density filler such as alumina particles.

When the size of a particle is given in terms of a single figure, this refers to an average dimension. For spherical particles this presents no problem, but with anisotropic particles the size is considered to be one-third of the sum of the three particle dimensions. For example, a fiber of asbestos might be 500 millimicrons long but only 10 millimicrons wide and thick. The size

$$\frac{500 + 10 + 10}{3}$$

of this particle would be 173 millimicrons, and hence within the limits of this invention.

The refractory particles must be dispersible in the molten metal mixtures. Dispersibility is a function of two properties, namely, the surface character of the particles and their geometry. The surface character giving dispersible particles is present when the refractory particles are subjected to contact with an active metal. Wettability can be assumed if, when a quantity of the refractory is added to a molten mass of the metal, it mixes with, and remains dispersed in, the metal. In this event the refractory is said to be wettable or metallophilic.

The geometry of the particles involves their size, shape, and packing density. The particles can be discrete, individual particles in the submicron range, or they can be aggregates of small ultimate particles. Thus, for instance, in the case of silica, aggregates up

to 500 millimicrons in size can be made up of ultimate spheroidal particles—say 17 millimicrons in diameter. Aggregates even larger than 1000 millimicrons can be used, the important consideration being the ease with which ultimate particles less than 500 millimicrons in size are formed from the aggregates in the molten mixture.

The aggregates can, for instance, be reticulated spheroida. Upon addition of such reticulated particles to molten metal and subjecting the mass to shear, the reticulated particles can be broken down into individual spheroids but the spheroids are still wet by the metal. This, the refractory materials added to the molten metal need not be in the form of discrete particles, provided they are dispersible to particles of a character as herein described, by such action as shearing.

The ease with which aggregates can be dispersed is indicated by their degree of coalescence and packing density. For instance, a very highly coalesced, densely packed aggregate might not readily disperse as desired, whereas a loosely packed material having a low degree of coalescence might quite readily disperse.

It has been found, according to the present invention that particulate refractory oxides, many of which are relatively inexpensive and readily available in the necessary finely divided form, can be wetted into molten metals if an active metal is present in sufficient proportion. The oxide, to be suitable, should be relatively non-reducible—that is, an oxide which is not reduced to the corresponding metal by hydrogen at temperatures below 1000° C, or by the metal in which it is embedded. Such fillers have a free energy of formation at 1000° C of more than 60 kcal./gm.at.O for the conditions used in making the low-melting products of the invention, and more than 90 kcal. for the conditions of making the high-melting products.

Mixed oxides can be used as fillers, particularly those in which each metal oxide in the mixed oxide conforms to the melting point and free energy of formation requirements above-stated. Thus, magnesium silicate,  $\text{MgSiO}_3$ , is considered as a mixed oxide of

$\text{MgO}$  and  $\text{SiO}_2$ . Each of these oxides can be used separately; also, their products of reaction with each other are useful. By “dispersion of an oxide” is meant a dispersion containing a single metal oxide or a reaction product obtained by combining two or more metal oxides. Also, two or more separate oxides can be included in the products of the invention. The term “metal oxide filler” broadly includes spinels, such as  $\text{MgAl}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$ , metal carbonates (which may decompose during the process of the invention to metal oxides), such as  $\text{BaCO}_3$ , metal aluminates, metal silicates such as magnesium silicate and zircon, metal titanates, metal vanadates, metal chromites, and metal zirconates. With specific reference to silicates, for example, one can use complex structures, such as sodium aluminum silicate, calcium, aluminum silicate, calcium magnesium silicate, calcium chromium silicate, and calcium silicate titanate.

Finely divided, naturally occurring minerals can be used as, for example, attapulgite, dispersed asbestos, talc, finely divided tourmaline, wollastonite, and other naturally occurring materials readily obtainable in a finely divided state. Some of these are highly hydrated materials and should be dehydrated before use. In exceptional cases where the object is to make a porous metal, some water of crystallization or constitution in the refractory can have a desirable effect, otherwise water and other volatile constituents are undesirable.

Colloidal metal oxide aquasols are particularly useful as a means of providing the fillers in the desired finely divided form, and hence are preferred. Zirconia sols are useful as starting materials. Particularly preferred are thorium sols prepared by calcining thorium oxalate and dispersing the resulting solid in dilute acid.

Typical single oxides which are useful as the filler include silica, alumina, zirconia, titania, magnesia, hafnia, and the rare earth oxides including thorium. A typical group of oxides suitable for use in both the high-melting and low-melting products of the invention, and their free energies of formation, is shown in the following table:

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| Oxide                          | $\Delta F$ at 1000° C. | Oxide                          | $\Delta F$ at 1000° C. |
|--------------------------------|------------------------|--------------------------------|------------------------|
| Y <sub>2</sub> O <sub>3</sub>  | 125                    | HfO <sub>2</sub>               | 105                    |
| CaO                            | 122                    | CeO <sub>2</sub>               | 105                    |
| La <sub>2</sub> O <sub>3</sub> | 121                    | Al <sub>2</sub> O <sub>3</sub> | 104                    |
| BeO                            | 120                    | ZrO <sub>2</sub>               | 100                    |
| ThO <sub>2</sub>               | 119                    | BaO                            | 97                     |
| MgO                            | 112                    | ZrSiO <sub>4</sub>             | 95                     |
| UO <sub>2</sub>                | 105                    | TiO                            | 95                     |

Additional oxides suitable for use in the low-melting products are:

| Oxide                          | $\Delta F$ at 1000° C. |
|--------------------------------|------------------------|
| TiO <sub>2</sub>               | 85                     |
| SiO <sub>2</sub>               | 78                     |
| Ta <sub>2</sub> O <sub>5</sub> | 75                     |
| V <sub>2</sub> O <sub>3</sub>  | 74                     |
| NbO <sub>2</sub>               | 70                     |
| Cr <sub>2</sub> O <sub>3</sub> | 62                     |

In attempts to add submicron oxide particles directly to molten metals having melting points above 720° C it is found that the oxide particles sinter and coalesce to such an extent that the very fine particle size is lost. Thus, it is not possible to add oxide particles directly to a molten high-melting metal and obtain a dispersion of submicron particles in the metal. In the present invention this problem is solved by first embedding the refractory oxide particles in an inactive metal, i.e., one which has an oxide which can be reduced to metal with hydrogen, and then adding this mastermix or masterbatch to molten metal.

#### *The Active Metal.*

Although the described oxides are useful as fillers in the processes of this invention, oxides per se are not wetted by metals having an oxide reducible by hydrogen below 1000° C and a  $\Delta F$  at 27° C below 88 kcal./gm. atom of oxygen. Hence, the surface at the interface requires modification before such oxides can be useful. This is accomplished by having present an active metal.

The observed results of having the active metal present can be explained on the basis

that the active metal reacts with the surface of the refractory oxide particles, thereby leaving them with a coating which is in a reduced valence state. With the most active metals, the process may merely involve a reaction of the metal with the surface of the oxide particle. However, with active metals of lesser activity, and particularly those which are incapable of reducing the oxide, a limited amount of oxygen is helpful in developing a metallophilic coating.

For purposes of the present invention, an active metal is defined as one having an oxide irreducible by hydrogen below 1000° C and a  $\Delta F$  at 27° C greater than 88 kcal./gm. atom of oxygen. This category includes beryllium, magnesium, aluminum, silicon, vanadium, titanium, tantalum, yttrium, zirconium, hafnium, niobium, the rare earth metals, lithium, sodium, calcium, barium and strontium. It will be noted that these elements stand above iron in the electromotive series. Preferably the active metal is one having a melting point above 1200° C.

In compositions containing a major proportion of active metal there is a correlation between the particular refractory oxide filler and the active metal to be used with it, in that the free energy of formation at 1000° C

of the refractory oxide should be greater than the corresponding free energy of formation of the oxide of the active metal. For example  $\Delta F$  for calcium oxide is 122 whereas aluminum oxide has a  $\Delta F$  of 104; hence, calcium oxide is a suitable refractory for dispersion in metal mixtures containing aluminum.

In one method for bringing together the active metal and the particulate refractory, one can vaporize an active metal, such as aluminum, magnesium, or calcium, onto the surface of an inorganic core of a refractory oxide such as silica, zirconia, or titania. This ordinarily is done at elevated temperatures, using care to avoid any oxidizing environment.

Effective for treating the surface of finely divided metal oxides in this manner to make them metallophilic by reduction are, for example, such active metals as magnesium, calcium, lithium, sodium, aluminum, or potassium. Of these, the alkali metals are not preferred because they react so readily with oxygen and water, including water vapor in the air, that reaction is difficult to control, and the resulting product is not generally stable. Compositions prepared using alkali metals, even when these are mixed with other metals, still retain this tendency to be readily oxidized. The alkaline earth metals suffer from somewhat the same disadvantage, although not quite to the same degree. For these reasons, active metals other than the alkali or alkaline earth metals are preferred.

When an active metal is used for modifying the surface of a refractory oxide core particle to make it metal-wettable and more readily dispersible, the active metal can reduce the oxide to one in which the metallic element combined with the oxygen is in a lower valence state, the lower oxide being more readily wettable. Alternatively, the active metal can form a surface coating around the core of refractory oxide. The coating can also consist of a layer of lower oxide, upon the outside of which there is a layer of the active metal.

The amount of active metal required to act as a reducing agent to reduce the surface of a refractory core is relatively small, on the molar basis, as compared to the total number of moles of material in the refractory or ceramic-like body under treatment. In general, from 4 to 20 mole per cent is usually sufficient; however, the amount required will vary directly with the surface area, and in the case where a finely divided, very high surface area material is used, this will require proportionally more of the active metal than when a relatively large particle is treated. In any event, one does not com-

pletely reduce the refractory body, but the proportion of active metal can, of course, be substantially more than the minimum required amount.

From a knowledge of the ultimate particle size or of the surface area and density of a given refractory body, one can calculate the mole percentage of the refractory oxide which is on the surface of the particle. From such a calculation, one can then determine the amount of active metal required as a reducing agent. It is preferred to use at least as much active metal as a reducing agent as would be required for coverage of the refractory particles to a thickness of 2 to 10 molecular layers or somewhat more.

As a specific instance of the minimum amount of active metal reducing agent to use for an amorphous, fine silica powder having spherical, 100-millimicron particles, one can calculate that the ratio of the silicon atoms on the surface of such particles to the total number of atoms in such particles is of the order of 2%. In working with a powder of this kind, one would use from 4 to 20 mole per cent of the active reducing agent, based on the total number of moles of silica in the silica powder being treated. With a silica powder in the form of dense, amorphous, spherical, 10-millimicron particles there would be in the order of 20% of the silicon atoms on the surface, and in this case there would be required ten times as much active metal, on a molar percentage basis. From these calculations, it can be seen that as the ultimate particles become smaller, a greater percentage of the total metal atoms present are on the surface of the particles. For this reason, a higher percentage of the active metal is required, and one prefers particles greater than about 10 millimicrons in diameter. Ultimate particles having a diameter in the range of 10 millimicrons to 150 millimicrons are specifically preferred.

#### *The Inactive Metal, Having Reducible Oxide.*

The metal with which the active metal and refractory oxide is mixed in compositions of this invention should have a melting point above 50° C, an oxide reducible with hydrogen below 1000° C, and a  $\Delta F$  at 27° C less than 88 kcal./gm. atom of oxygen. Mercury, having a melting point below 50° C, is unsuitable, since it has no utility as a material of construction.

This category of relatively "inactive" metals consists of iron, cobalt, nickel, molybdenum, tungsten, chromium, copper, silver, gold, cadmium, lead, tin, bismuth, and indium. Generally, they are metals which are used as materials of construction or as constituents of alloys used for this purpose.

*Surrounding the Refractory Oxide with  
High-Melting Inactive Metal.*

In the process for making products having melting points above 720° C, having selected a refractory oxide filler, an inactive metal, and an active metal as above described, one surrounds the filler particles with the inactive metal and then dilutes the inactive metal with an active metal while maintaining the filler as separate particles.

The method used for surrounding the refractory oxide particles with inactive metal must be one which will not cause the particles to agglomerate or to grow to a size outside the stated range. With high-melting, inactive metals such as iron, cobalt, nickel, molybdenum, chromium and tungsten this poses a problem, particularly with any but the most refractory of fillers. Accordingly, in a preferred aspect of the invention the inactive metal-filler concentrate is prepared by precipitating a compound of the metal, in which the metal is in an oxidized state, in contact with the dispersed filler particles, and then reducing the metal compound to the corresponding metal, as by treating it, after drying, with hydrogen at elevated temperature.

The precipitated compound of the inactive metal can be the oxide, hydroxide, hydrous oxide, oxycarbonate, or hydroxycarbonate. Since these compounds, as precipitated, usually contain varying amounts of water, they can be referred to generally as hydrous, oxygen-containing compounds of the metal.

The precipitated inactive metal compound can be one of a single metal or of two or more metals. For example, the hydrous oxides of both nickel and cobalt can be deposited around a filler. In the latter case, an alloy of cobalt and nickel is produced directly, during the reduction step. In similar manner, alloys of iron, cobalt, or nickel, for example, can be prepared with other metals which form hydrogen-reducible, hydrous, oxygen-containing compounds. Thus, alloys with copper, molybdenum, tungsten, and rhenium can be prepared by codepositing two or more oxides of the selected metals on the filler particles.

The hydrous, oxygen-containing compound can be precipitated from solutions in which it is present as the corresponding soluble salt. Preferably, the salt is a metal nitrate, although metal chlorides, sulfates, and acetates can be used. Ferric nitrate, cobalt nitrate, nickel nitrate, ammonium molybdate, and sodium tungstate are among the preferred starting materials.

Methods for precipitating oxygen-containing metal compounds from solutions of the corresponding metal salts are well known in the art and any such method can be used. For instance, an alkali can be added to a solution of the metal nitrate. When, on the

other hand, the metal is in the form of a basic salt, such as sodium molybdate, precipitation can be effected by acidifying.

A preferred method for surrounding the filler particles with the oxygen-containing compound of inactive metal is to coprecipitate the filler particles from a colloidal aquasol simultaneously with the precipitation of the inactive metal compound. One convenient way to do this is to add, simultaneously but separately, a solution of the soluble metal salt, a colloidal aquasol containing the filler particles, and an alkali such as sodium hydroxide, to a heel of water. Alternatively, a dispersion containing the filler particles can be used as a heel and the metal salt solution and alkali added simultaneously but separately thereto.

During such a coprecipitation process certain precautions are preferably observed. It is preferred not to coagulate or gel the filler particles. Coagulation and gelation are avoided by working in dilute solutions, or by simultaneously adding the filler and the metal salt solution to a heel.

The filler particles should be completely surrounded with the precipitated, reducible inactive metal compound, so that when reduction occurs later in the process, aggregation and coalescence of the filler particles is avoided. In other words, the particles of the filler are discrete and not in contact, one with another, in the coprecipitated product. Vigorous mixing and agitation during the coprecipitation helps to insure the desired result.

After depositing the insoluble inactive metal compound on the filler, any salts present are removed, as by washing. When one uses an alkali such as sodium hydroxide, potassium hydroxide, lithium hydroxide, ammonium hydroxide, or tetramethylammonium hydroxide to effect precipitation, salts such as sodium nitrate, ammonium nitrate or potassium nitrate are formed. These should be removed. One of the advantages of using the nitrate salts in combination with aqueous ammonia is that ammonium nitrate is volatile and therefore is easily removed from the product. However, the tendency of many metals, such as cobalt and nickel, to form amine complexes is a complicating reaction in this case. By carefully controlling the pH during coprecipitation, these side reactions can be avoided.

A very practical way to remove salts is by filtering off the precipitate and washing it on the filter or repulping the filter cake and again filtering.

After removing soluble salts the product is dried, preferably at ultimate temperatures above 100° C. Alternatively, the product can be dried, and the dry material suspended in water to remove the soluble salts, and the product thereafter redried.

The relative amount of insoluble inactive

metal compound deposited upon the filler particles can be varied over wide limits. Volume loadings as high as 50 per cent, that is, one volume of oxide for each volume of metal present, can be successfully used, but such products are often pyrophoric. Even heating to 1000° C after reduction does not completely eliminate this problem.

The pyrophoric tendency is minimized as the volume loading is decreased. In the range of 40 to 50 volume per cent of filler, it is advisable to protect the modified metal in an inert atmosphere (hydrogen, argon or helium) until the material is used in the casting process. At 30 volume per cent, one can usually sinter the modified metal mass sufficiently that it can be handled in air, prior to its addition to molten metal.

The amount of precipitated inactive metal compound which it is desired to deposit upon the filler will vary somewhat with the particle size of the filler and especially with its surface area. Thus, with the smaller sizes of filler particles, having surface areas greater than  $200/D \text{ m}^2/\text{g}$ ,  $D$  being the density of the filler in  $\text{g}/\text{ml}$ , volume loadings of from 0.5 to 5 per cent are preferred. With relatively large particles—those, for example, in the size range of 100 millimicrons—one can use volume loadings near the upper end of the ranges above mentioned.

Having deposited on the filler particles the precipitate of compound of inactive metal in the oxidized state, and washed and dried the product, the next step is to reduce the inactive metal compound to the metal. This can be done conveniently by subjecting the coated particles to a stream of hydrogen at a somewhat elevated temperature. The temperature throughout the entire mass must not be allowed to exceed the sintering temperature of the filler particles. One way to accomplish this is to place the product in a furnace at a controlled temperature and add hydrogen gas slowly; in this way, the reduction will not proceed so rapidly that large amounts of heat are liberated causing the temperature to get out of control.

The hydrogen used in the reduction can be diluted with an inert gas such as argon to reduce the rate of reaction and to avoid "hot spots." In this way the heat of reaction is carried away in the gas stream. Alternatively, the temperature in the furnace can be slowly raised into the range of 500 to 1000° C while maintaining a flow of hydrogen over the product to be reduced.

In addition to or instead of hydrogen, other reducing gases such as carbon monoxide, or methane and other hydrocarbon gases can be used as the reducing agent. In any case, it is important to control the temperature during reduction, not only to avoid premature sintering as above mentioned, but also so that excessive reaction

will not occur between the reducible inactive metal compound and the filler oxide prior to complete reduction of the inactive metal compound.

Reduction should be continued until the inactive metal compound is essentially completely reduced. When reduction is nearing completion, it is preferred to raise the temperature to the range between 700 and 1300° C to complete the reaction, but care must be taken not to exceed the melting point of the reduced metal. During the reduction process very fine metal grains are formed. These tend to fuse and grow, but their ultimate size is restricted because of the presence of the filler particles. Thus, the size of grains obtained in this way is usually less than 10 microns.

Reduction should be carried out until the oxygen content of the mass is substantially reduced to zero, exclusive of the amount of oxygen originally introduced in the form of the oxide filler material. In any case, the oxygen content of the product, exclusive of the oxygen originally introduced in chemically combined form in the filler, should be in the range of from 0 to 0.5% and preferably from 0 to 0.1%, based on the weight of the product.

The analysis for oxygen can be done by many methods with which the art is familiar, one such method being vacuum fusion as described by R. A. Yeaton in *Vacuum*, Vol. 2, No. 2, page 115, "The Vacuum Fusion Technique as Applied to Analysis of Gases in Metals."

Oxygen, other than that combined with the filler, may interfere with the function of the active metal, by reacting with the active metal to yield active metal oxide. For this reason the oxygen level should be maintained in the range above stated until after mixing with the molten, active metal is complete.

After the reduction reaction is complete, the resulting powder is sometimes pyrophoric. Therefore, it is preferred to cool the mass and maintain it in an inert atmosphere until it has been sintered to a surface area of  $2 \text{ m}^2/\text{g}$  or less or until it has been diluted with the active metal and used in the casting process.

#### *The Proportion of Active Metal.*

In compositions of this invention the active metal is present in at least the minimum proportion which prevents drossing out of the refractory oxide when the composition is maintained in a quiescent molten state for  $\frac{1}{2}$  hour. A proportion of at least 4 mol per cent, based on the refractory oxide, accomplishes this result. It has been found that "drossing" out or "slagging" out is a measure of lack of bonding of the metal matrix to the dispersed refractory oxide par-

5 ticles. A molten metal mixture containing refractory oxide can be vigorously agitated or intensively mixed to such a degree that the oxide appears to be homogeneously dispersed. However, if there is insufficient active metal to give the desired improved bonding in the final product, this fact can be readily ascertained by permitting the molten mixture to stand quiescent for  $\frac{1}{2}$  hour. If any substantial amount of the refractory oxide floats to the top or settles to the bottom, the proportion of active metal is inadequate and should be increased.

10 The presence or absence of drossing out can readily be determined by freezing a sample, after  $\frac{1}{2}$  hour of quiescent standing as a molten mixture, to form an ingot, and examining its homogeneity of composition.

15 The homogeneity of distribution of the refractory oxide particles can easily be ascertained by ordinary procedures of mechanical sampling and analysis. Sections of the solid metal ingot just described are taken from the outer portions, from the center, and from the top, the bottom, and the middle, in such a manner as to give samples of the composition from all of the several areas of the ingot. These samples are obtained by ordinary metal working procedures, such as sawing or chiseling. The samples are then analyzed by chemical methods, by metallographic examination (such as by light and electron microscopes) by a measurement of the conductivity of the metallic phase, by a determination of density, or by radiotracer techniques, in the event that the filler particles are radioactive (e.g., thoria or uranium oxide), or by any other suitable procedure for determining the chemical composition of a system.

20 Products of this invention in which no drossing out of filler particles has occurred are characterized by having substantially the same chemical compositions in each portion of the cast ingot. If extensive phase separation has occurred, areas from the oxide-rich portion of the ingot will analyze very much higher in the chemical constituents of the oxides than areas taken from other portions of the ingot. If the oxide concentration in any single major area of the ingot is more than 50% greater than that of any other major area, drossing out is considered to have occurred.

#### 55 *Process for Making the Low-Melting Compositions.*

60 Compositions having melting points of from 50 to 720° C are produced by processes which include the step of mixing the refractory oxide particles with a molten mass of metal having an oxide which is reducible by hydrogen below 1000° C, the mixing being carried out at a temperature of from 50 to 720° C and while there is present at least

65 enough active metal to prevent drossing out of the refractory. The intensity of mixing is sufficient to disperse the refractory into substantially discrete particles 5 to 500 millimicrons in average dimension.

70 A variety of methods can be employed for effecting the presence of active metal in the molten metal mixtures. One method is to mix the finely divided refractory material with the molten metal to be modified, said mixture containing small amount of the active metal. For example, one can use a magnesium-lead alloy containing 1 to 2% magnesium. The finely divided powder, such as finely divided silica powder is floated on top of this molten metal, and on mulling, the magnesium-lead alloy wets the powder, and the powder becomes dispersed in the metal. As much as 5, or even 7 or 8%, of silica powder can be added to a molten alloy. In this instance a wettable surface on the silica is formed in the molten metal bath in situ, and no drossing out of the silica occurs. The molten lead thus is the metal which is modified by the surface-coated silica. Fine silica powders which are used in this type of process contain particles which are of the order of 100 millimicrons in diameter. Other metals which can be used in place of lead are, for instance, molten tin, cadmium, cadmium-zinc alloys, and alloys containing zinc, lead and tin.

90 Before incorporating the refractory oxide particles into the molten metal mixtures the surfaces of the particles can be made metallophilic by treating them with the vapor of an active metal. For instance, fine silica powder can be treated with calcium or sodium vapor in an inert atmosphere at elevated temperatures and preferably under reduced pressures. This should be done under such conditions that the calcium metal reacts with the silica powder, presumably through the formation of calcium-oxygen-silicon bonds, probably with outer valences of the calcium being unsatisfied, and possibly also leaving partly reduced silicon atoms on the surface of the particles as illustrated in Figure 1. The result of such treatment is that the powder becomes metallophilic.

105 It is important to carry out the mixing in an inert atmosphere to prevent excessive oxidation of the active metal. Argon is particularly suitable.

115 In one aspect of the invention, homogeneous mixing of the refractory oxide with the molten metals is facilitated by having present a limited amount of oxygen. This causes the refractory oxide to wet into the metal mixture more readily, apparently by depositing a coating of compounds of the metals in a reduced valence state on the surface of the refractory particles. Thus, an oxide refractory can be coated with an oxide of a metal, this coating being in a reduced

valence state. By a "reduced valence state," we mean that the ratio of the metal to oxygen in the coating is substantially greater than the ratio of metal to oxygen which is normally found in the stable oxide compounds of said metal. In other words, an excess of metal is present in the coating.

When making products having melting points in the range of 50 to 720° C, finely divided oxides such as alumina, silica, zirconia, magnesia, thoria, titania, chromia, and the like, can be mixed with molten metals such as zinc, indium, aluminum, cadmium, or mixtures of such metals, such as zinc and indium, optionally in the presence of a limited amount of oxygen. Similarly, when making products having melting points above 720° C, powdered dispersions, in inactive metals, of finely divided oxides such as alumina, zirconia, magnesia, thoria, and the like can be mixed with molten metals such as niobium, tantalum, titanium, rare earth metals, silicon, or aluminum, or mixtures of metals such as niobium and titanium, optionally in the presence of a limited amount of oxygen.

In the case of certain metals, like zinc, the reaction can be carried out in air, but the precaution should be taken that the temperature of the molten zinc is maintained at or near the melting point, since if the temperature is allowed to get too high, excessive oxidation will occur and the entire mass of zinc can become oxidized. The oxidation must be carefully controlled, so that an oxide of a reduced valence state which acts as a wetting agent is formed, but the normal oxide is not formed, at least in appreciable amounts.

#### 40 *Casting the Molten Mixtures.*

As the final step in processes of the invention, the refractory oxide-filled molten metal is cast—that is, it is cooled and solidified. The art is familiar with casting techniques, and any of these can be used.

#### *Low-Melting Products Having High Dispersed Oxide Content.*

It is possible to prepare rather concentrated dispersions of oxides in metals according to this invention. Thus, volume loadings up to 50 or more per cent of an oxide refractory in a low-melting molten metal and up to about 30 per cent in a high-melting metal can be achieved. The loading which can be obtained in any system will vary with the density of the refractory and metal, and the surface area and state of aggregation of the refractory. Ordinarily, for final use, one will want to have final compositions containing less than 10% refractory. In practice, this can be achieved by preparing a "masterbatch" of an oxide refractory in a mixture of active and inactive metal, and later diluting this

with additional metal or alloy to prepare the final composition. Compositions comprising such dispersions of refractory oxide particles in low-melting metals are an especially preferred aspect of the invention.

In this manner, for example, a masterbatch of silica and indium can be prepared, and this masterbatch can later be diluted with such metals as molten lead, tin, bismuth, or alloys of these or even other metals, in order to produce lead-indium-silica compositions. Masterbatches can be prepared directly from alloys. In a similar way, one can, for example, prepare masterbatches containing: (a) magnesium-alumina, (b) magnesium-zirconia, and (c) zinc-thoria. Magnesium-zirconia masterbatches can be used for further dilution with aluminum, copper, their alloys, or other similar metals. Masterbatches containing zirconia are especially useful for further dilution with the ferrous metals or their alloys. Masterbatches containing thoria are also similarly useful for further dilution with the high-melting metals.

As especially useful composition of this type, thus, is a masterbatch comprising a low-melting metal and a metal oxide. It has been observed that oxides having a high surface area are easily sintered, i.e., the coalescence between the ultimate particles increases rapidly on heating. For example, fine silica powders having particles in the size range corresponding to 25 to 250 m $\mu$  are affected at temperatures in the range of 200–600° C., even though the melting point of amorphous silica is listed as 1600° C. (Note that the coalescence of silica powders can readily be determined by the method given in U.S. 2,731,326, column 12, lines 24 and following.) Thus, if one attempts to incorporate fine silica into molten metals having melting points above about 200° C., coalescence of the fine powder may occur, with the result that the effective particle size of the silica may be increased and the beneficial effects of the small particle size may be lost. For this reason, masterbatches of silica in low melting metals like indium are especially desirable. Once the silica is well dispersed in the indium, it can then be further diluted with other, higher-melting metals, especially active metals, in the molten state. Since the silica particles are no longer in contact, sintering cannot occur.

In like manner problems attributable to sintering of silica particles can be abated by having the silica initially present in crystalline form. For example, one can employ a dispersion of colloidal quartz, instead of the amorphous silica above mentioned.

Zinc is a readily available, low cost metal, having a melting point of 420° C. For these reasons, zinc is especially useful in preparing masterbatches of zinc-zirconia, zinc-alumina, and even zinc-silica. In the latter case, care

should be used to select a silica which will not readily coalesce during the process of incorporation into the zinc. In this case, such precautions should be exercised as using relatively large silica particles, particularly crystalline silica, say in the size range of 25 to 250 millimicrons, and minimizing the time required during wetting and dispersion. Masterbatches of zinc and metal oxides, especially zinc-alumina and zinc-zirconia, are useful for mixing with higher melting metals, such as magnesium, aluminum, iron, cobalt, nickel, copper, chromium, and titanium, in order to produce alloys containing highly dispersed, finely divided oxide particles.

Other metals besides zinc which are especially useful for making metal-metal oxide masterbatches include indium, tin, lead, cadmium, and bismuth. In addition, low-melting alloys such as Lipowitz metal (50% Bi, 27% Pb, 13% Sn, 10% Cd), Woods metal, or Rose metal, are useful for making masterbatches. Aluminum-magnesium alloys are also useful in making masterbatches, an aluminum-magnesium-zirconia product being especially preferred. In general, metals or alloys having a melting point in the range from 50° to 500° C are useful in making masterbatches, as above described. It is desired to have a metal which is solid at room temperature, in order to facilitate handling such as extrusion of solid pieces.

#### *Special Considerations as to Products.*

In some cases, one would attempt to match the coefficient of expansion of the oxide with the coefficient of expansion of the metal alloy in which it is included. The purpose of this is to avoid having strains set up in the resulting metal-metal oxide compositions when thermal changes occur in the final system. The effect of thermal strains can be minimized by using very small particles, for example, using particles in the size range of from 25 to 250 millimicrons, which corresponds to a surface area in square meters per gram from  $24/D$  to  $240/D$ , where  $D$  is the density of the refractory in grams per milliliter.

Another consideration is the density of the refractory core used in these compositions. Here again, it is sometimes desirable to match the density of the refractory core as closely as possible with that of the metal or metal alloy involved. The reason for this is that, when there are gross density differences, and particularly with larger particles, there is a tendency of the particles to sink or float, depending on whether they are more or less dense than the metal in which they are found. This tendency to settle or to float increases the difficulties of obtaining homogeneity in dispersions of liquid metals, and for this reason, matching of densities is sometimes desirable. However, when particles are

dispersed according to the invention there is very little tendency toward either floating or settling. Successful welding of metals reinforced according to this invention is almost impossible if the filler is not well wetted and dispersed.

In the process as above described, one obtains best results with refractory powders which are smaller than about  $\frac{1}{2}$  micron, and, specifically, the surface range which is preferred is from  $24/D$  to  $600/D$   $m^2/g.$ , where  $D$  is the density of the core of the refractory being used. Particles smaller than this are difficult to handle and to wet. Moreover, they tend to sinter or fuse to non-dispersible masses during the process of incorporation into the molten metal, and hence should only be used if care is exercised to avoid temperatures at which fusion or sintering occurs. With larger particles, i.e., those having a surface area less than  $24/D$   $m^2/g.$ , the benefits obtained relating to the strength of metals are considerably less than those obtained with smaller particles.

In processes of the invention, dispersion is as important as wetting. Having obtained compositions comprising a masterbatch or an initial mixture of a refractory wetted into a molten metal, it is then necessary to obtain a suitable state of dispersion. Most oxide refractories will not spontaneously disperse, even after they are wetted. Wetting under simple mixing condition is therefore often not sufficient to obtain dispersion. Dispersion can be achieved by subjecting the system to very high shear forces, for example, by hot or cold extrusion of the composition, milling in a Banbury mixer, colloid milling, or using roll milling techniques, similar to those used in ink or rubber milling, and this can be advantageously done at a temperature at or near the melting point of the metal or metal alloy in question. In these instances, it is expected that appropriate materials of construction will be used to contain the compositions in question. Whichever technique is used, it is desirable that essential homogeneity of the refractory-metal composition be obtained and maintained during the cooling operation, since heterogeneities may introduce areas of weakness and strain points in the resulting metal compositions. Products which are relatively homogeneous both with respect to particle size of the refractory and to the state of dispersion are preferred.

The extent of dispersion can be determined by applying Stoke's law, see, for example, Ware, "Chemistry of the Colloidal State", John Wiley and Sons, Inc., 1936, 2nd Edition, p.24 and following. By maintaining a metal-metal oxide composition at a temperature above the melting point of the metal phase, and measuring the rate of separation (due to settling or floating) of the oxide phase, it is possible to determine the particle size

distribution. The preferred products, prepared according to this invention, have at least 80% of their particles dispersed to a state which corresponds to a size less than 1 micron.

5 The particle size of the oxide as it is added or wetted into the metal may not correspond to the particle size which exists in the metal. Thus, aggregation may occur with the result that the effective particle size may be larger than expected. Therefore, the application of a dispersing technique during or after wetting is needed.

10 In order to obtain metal-metal oxide compositions which can be effectively handled in usual metal-metallurgical operations, such as casting and welding, it is important that both wetting and dispersion be achieved. Products of this invention can be melted in an inert atmosphere, and there will be no gross separation or dewetting in a period of 20 30 minutes.

25 Using techniques above described, metal structures can be produced by mixing the refractory with a molten metal. Unique characteristics are displayed even in the molten mixture, in that certain metals become pasty at temperatures where they would otherwise be relatively mobile liquids. Novel properties are also manifest when the molten metals are cooled and solidified.

30 The preferred upper limit of volume loadings of refractory oxide in the final metal products (as distinguished from masterbatches) is 50% by volume, and in most instances one would use from 1 to 10% by volume. Even as little as a tenth of a per cent has beneficial effects in some instances.

#### *The Metal Products.*

40 Metals modified by having dispersed therein finely divided, wetted refractory particles as above described have remarkably improved properties. The high-temperature strength of the high-melting metals is increased, and at the same time the impact strength and ability to resist stress rupture is increased. The structural metals are thus given enhanced utility, especially in such high-temperature uses as in turbine blades, boiler tubes, and the like. The active metals, such as aluminum and magnesium, are given increased utility as structural materials.

50 The importance of particle size is evident when one considers the balance of properties which can only be obtained with very small particles. Thus, one can reduce creep in metal systems by the conventional cermet, which is a combination of metal with refractory, in which the refractory is present as large particles. However, in such systems, the ductility and impact strength is largely lost. Now according to this invention, it is possible to reduce creep, and at the same time maintain ductility and impact strength to a considerable degree.

65 The character of the dispersed refractory oxide particles in the metal products can be demonstrated, using electron microscope and replica techniques wherein the surface of a metal piece is polished, a carbon layer is deposited on the polished surface, and the metal is removed, as by dissolving in an acid. An electron micrograph of the remaining carbon film shows the nature of distribution and degree of aggregation of the refractory oxide particles in the metal.

70 Another property of products of this invention is corrosion resistance. In the conventional oxide cermets, corrosion resistance, particularly oxidation resistance at elevated temperatures is poor. It has now been found that in the case of the products of this invention, in which small particles are introduced into and wetted by the continuous metal phase, there is little or no sacrifice in corrosion resistance, and in some instances, corrosion resistance is improved.

80 A particularly advantageous characteristic of the low-melting metal products of this invention is their fatigue strength. Metals containing macroscopic particles of refractories ordinarily have poor fatigue strength, but when the refractory particles are as small, well dispersed, and strongly bonded to the metal as is the case in the present metal products, the fatigue strength is not impaired and is generally increased.

90 Similarly, it might be expected that the oxide inclusions of the metal products of this invention might cause a lowering of the ability of the metal to resist crack propagation. Not only is this not the case, but on the contrary, the crack-propagation resistance is actually increased in preferred products of the invention.

#### *EXAMPLES.*

105 The invention will be better understood by reference to the following illustrative examples, of which 1 to 25 are concerned with low-melting products and 26 and those following it are concerned with high-melting products.

#### *EXAMPLE 1.*

110 This example relates to modification of a zinc-cadmium alloy in accordance with the invention. Calcium metal is used as a reducing agent to effect wettability of a finely divided silica powder in the alloy.

115 A silica aquasol, prepared as described in specification No. 667,154, was deionized with ion-exchange resins and dried to a fine powder. This powder had a surface area of 30 m<sup>2</sup>/g, a density of 2 g/ml, and a particle size of approximately 100 millimicrons. The powder was dried at a temperature of 110° C. in an oven. The resulting powder had a coalescence factor, determined as in U.S. patent 2,731,326, col. 12, 1.24 et seq., of 1.4%.

120 A zinc-cadmium alloy, composed of 82.5%

cadmium 17.5% zinc by weight, was placed in a dry-box containing an argon atmosphere. To this zinc-cadmium alloy was added 1% by weight of calcium metal. The resulting material was heated to a temperature of about 450° C. To this molten metal, the fine silica powder was added. The resulting metal-silica was mullied in a mortar with a pestle, whereupon the silica was readily wetted into the molten zinc-cadmium alloy. The composition produced was a metal containing dispersed therein 5% silica. The molten mixture, upon quiescent standing for ½ hour, showed substantially no drooping out of the silica. This material was then cooled to solidify it. The silica remained dispersed in the metal.

#### EXAMPLES 2—9.

Other compositions prepared as outlined in Example 1 and containing the reducing agents and refractory materials in the indicated proportions, are described in Table I.

TABLE I

| Example | Alloy                      | Wetting Agent (%) | Refractory Filler (%)             |
|---------|----------------------------|-------------------|-----------------------------------|
| 2       | Cd 82.5%<br>Zn 17.5%       | Ca 2%             | Al <sub>2</sub> O <sub>3</sub> 4% |
| 3       | Cd 82.5%<br>Zn 17.5%       | Ca 2%             | TiO <sub>2</sub> 4%               |
| 4       | Sn 50%<br>Pb 30%<br>Zn 20% | Ca 1%             | SiO <sub>2</sub> 9%               |
| 5       | Sn 82%<br>Zn 18%           | Ca 2%             | SiO <sub>2</sub> 12%              |
| 6       | Cd 82.5%<br>Zn 17.5%       | Ca 2%             | Talc 4%                           |
| 7       | Mg 2%<br>Pb 98%            | Mg 1.95%          | SiO <sub>2</sub> 2%               |
| 8       | Mg 2%<br>Pb 98%            | Mg 1.9%           | Al <sub>2</sub> O <sub>3</sub> 4% |
| 9       | Li 0.5%<br>Pb 99.5%        | Li 0.49%          | SiO <sub>2</sub> 2%               |

In each of the above examples the refractory filler was readily wetted by, and easily dispersed in, the molten metal, and remained dispersed upon cooling of the metal to solidify it. In all instances the metals had improved strength at temperatures near their melting points.

#### EXAMPLE 10.

This example illustrates the preparation of a masterbatch active metal-filler mixture of the invention.

To a molten aluminum alloy (65% Al, 35% Mg) maintained at 475° C. under an argon atmosphere, zirconia (165 m<sup>2</sup>/g.) was added with rapid mechanical agitation. Oxygen was simultaneously introduced into the reactor atmosphere at a partial pressure of 1—2 mm. resulting in immediate wetting of the zirconia powder by the melt. Zirconia was incorporated in the alloy until a loading of 2% by weight was attained, with an accompan-

ing gain of 0.07% oxygen by weight corresponding to one monomolecular layer of oxygen based on the alumina.

The resulting filled billet was then extruded in order to disperse the zirconia. One part of the extruded alloy was then diluted by comelting with six parts of aluminum metal, yielding an alloy suitable for mixing with inactive metals in accordance with the invention.

#### EXAMPLE 11.

To 100 g. of a molten alloy of cadmium and zinc (82.5% Cd, 17.5% Zn) in a crucible, 0.5 g. of calcium metal was added. When solution of the calcium was attained, 1.4 g. of "Cab-o-sil" [Godfrey L. Cabot, Inc., 0.015—0.020 micron particle size silica, surface area (by nitrogen adsorption) of 175—200 square meters per gram] was floated on top of the alloy, then stirred into the molten mass. After stirring for 30 minutes, a finely

divided, dense, metallic powder was obtained while the crucible temperature remained at 350° C., a temperature at which the cadmium-zinc-calcium alloy would ordinarily be fluid (melting point of 82.5% Cd., 17.5% Zn eutectic lies at 263° C.). The entire process was carried out in a dry box under an argon atmosphere.

The dense, metallic powder obtained, which was stable in air, was then molded under a pressure of 20,000 p.s.i. at a temperature of 250° C. (well below the melting point of the alloy). A dense, metallic-appearing billet was obtained which was easily machined. Such a powder, containing silica uniformly dispersed, could thus be pressed into useful shapes which could be handled and machined by conventional metallurgical techniques.

#### EXAMPLE 12.

To a molten magnesium-indium alloy containing 0.3% magnesium and maintained at 190–225° C., "Cab-o-Sil" was wet into the molten alloy under 20 mm. oxygen partial pressure with rapid mechanical stirring in a closed system. One per cent by weight of silica was thus introduced into the alloy with an accompanying 0.18% of oxygen corresponding to 2.8 monolayers of oxygen on the silica. This metal-oxide preparation was then used as a masterbatch and was subsequently diluted with lead to 1 volume % silica in the alloy. After compaction and six hot extrusions at 200° C. of a 1" dia. slug through a 1/16" dia. hole, using a pressure of 25,000 psi, (the extrudate, after each extrusion being reformed, under pressure, into a 1" dia. slug), the silica filled lead had improved creep resistance and increased tensile strength. By using more or less of a similar masterbatch, containing 100  $\mu$ m silica volume loadings of 0.1 0.5 and 2.0 were made.

#### EXAMPLE 13.

To a molten calcium-indium alloy agitated mechanically and containing 0.5% calcium maintained at 190–225° C., amorphous silica (32.9 m<sup>2</sup>/g.; 100  $\mu$  average particle diameter) was wet into the alloy under 15 mm. oxygen partial pressure in a closed system until the silica content reached 4.0% by weight. In the process, 0.09% by weight of oxygen was incorporated into the filled alloy corresponding to 3 monolayers of oxygen on the silica. This composition was then employed as a masterbatch for filling and strengthening lead, as described in Example 12.

Examples 14 to 23 illustrate the preparation of active metal-refractory filler masterbatches of the invention suitable for mixing with inactive metals.

#### EXAMPLE 14.

To molten zinc maintained at 475° C under an oxygen partial pressure of 447 mm.

and agitated by hand mulling, amorphous silica (32.9 m<sup>2</sup>/g., 100  $\mu$  average particle diameter) was added until the silica content reached 2% by weight. Oxygen consumed during the process corresponded to 0.26% by weight or 10 monolayers of oxygen on the silica.

After hot extrusion, the filled zinc had improved tensile strength at temperatures near its melting point.

#### EXAMPLE 15.

To molten zinc maintained at 475° C under an oxygen partial pressure of 159 mm. and agitated by hand mulling, 0.5% by weight of alumina ("Alon C", Godfrey Cabot Co., 93 m<sup>2</sup>/g., 10–40 m $\mu$  average particle diameter) was added to the melt. The oxygen used in the process corresponded to 0.4% by weight of 22 monolayers of oxygen on the alumina.

After hot extrusion, the filled zinc had improved tensile strength at temperatures near its melting point.

#### EXAMPLE 16.

To molten zinc maintained at 475° under an oxygen partial pressure of 159 mm. and agitated by rapid mechanical stirring, zirconia (196 m<sup>2</sup>/g.) was added to a concentration of 2%. The oxygen consumed corresponded to 1.4% by weight or 10 monolayers of oxygen on the zirconia.

After repeated hot extrusion of a 1" dia. slug through a 1/4" dia. hole, (the extrudate, after each extrusion, being reformed into a 1" dia. slug), the filled zinc had improved tensile strength at temperatures near its melting point. Such compositions as this can be further diluted with other metals.

#### EXAMPLE 17.

To a molten aluminum alloy (65% Al, 35% Mg) maintained at 485–500° C under an argon atmosphere containing 0.002% oxygen, dispersible zirconia powder consisting of dense ultimate particles about 7 millimicrons in size and approximately cubical in shape, with a surface area of 179 m<sup>2</sup>/g., is added rapidly with agitation until a weight loading of 11.6% (5.0% by volume) is attained.

After freezing, the filled billet is then extruded in order to disperse the zirconia. This masteralloy containing the zirconia in a dispersed state is then diluted by co-melting with aluminum metal. In this manner, one part of the masteralloy described above is diluted with ten parts of aluminum, yielding an alloy with improved tensile strength at elevated temperatures.

#### EXAMPLE 18.

To molten aluminum maintained at 675–700° C under an argon atmosphere, zirconia (179 m<sup>2</sup>/g.) was added with rapid mechanical agitation. Oxygen was simultaneously introduced into the reactor atmosphere at a partial pressure of 1 mm. result-

ing in immediate wetting of the zirconia powder by the melt. The zirconia was added in this manner until a weight loading of 0.6% (0.003 by volume) was attained.

After cooling, the filled aluminum billet was extruded to disperse the zirconia. By this procedure a filled metal billet having striking improvements in elevated temperature creep properties can be obtained.

#### EXAMPLES 19—23.

A series of reinforced aluminum alloys containing magnesium as a wetting agent and

zirconia as a filler was prepared by maintaining the molten alloy at 680—720° C under an argon atmosphere, and simultaneously introducing zirconia and oxygen (at low concentrations, 0.002%) to the reactor atmosphere. Wetting of the zirconia powder was rapid and the wetting process was accelerated by mild agitation of the melt. In this manner, the following alloys were prepared containing the wetting agent and zirconia filler in the indicated proportions:

| Volume %<br>of Filler, ZrO <sub>2</sub> | Weight %<br>of Filler, ZrO <sub>2</sub> | Weight %<br>of Wetter (Mg) |
|---|---|----------------------------|
| 2.5                                     | 5.0                                     | 0.47                       |
| 1.0                                     | 2.0                                     | 0.20                       |
| 0.5                                     | 1.0                                     | 0.10                       |
| 0.1                                     | 0.2                                     | 0.02                       |
| 0.05                                    | 0.1                                     | 0.01                       |

After extrusion, the filled aluminum alloys containing the zirconia in a dispersed state are observed to have striking improvements in elevated temperature properties. Particularly beneficial improvements in tensile strength and creep are observed.

#### EXAMPLE 24

This example describes the preparation of an alloy of copper and aluminum containing 0.7 volume per cent of alumina (Al<sub>2</sub>O<sub>3</sub>) in the form of a colloidal dispersion.

The first step in the preparation of this alloy was to prepare a dispersion of colloidal alumina in copper metal. This was done by diluting 652 parts by weight of a 5% solution of colloidal alumina monohydrate fibrils having a specific surface area of about 300 m<sup>2</sup>/g, and a fiber length of about 250 millimicrons, to a total volume of 5 liters with distilled water. Separately, 2370 grams of copper nitrate trihydrate was dissolved in 5 liters of distilled water, and 3600 cc. of 5N ammonium hydroxide solution was diluted to a volume of 5 liters. These three solutions were run simultaneously and at equal rates into the mixing zone of a reactor equipped with a high-speed stirrer. By means of this technique, the colloidal alumina was evenly dispersed throughout a matrix of copper hydroxide.

The precipitated copper hydroxide containing the dispersed colloidal alumina was filtered, washed, and reduced in a tube furnace with hydrogen until substantially all of the oxygen was eliminated. Analysis

of the resulting reduced metal powder containing dispersed colloidal alumina within it showed that the sample consisted of 88.7% copper and 9.7 Al<sub>2</sub>O<sub>3</sub>, this corresponding to a loading of 19.6% Al<sub>2</sub>O<sub>3</sub> in copper by volume.

A portion of this material was dissolved in acid and electron micrographs were run on the resulting solution after dialyzing out the acids and salt left by the dissolution of the copper. The electron micrographs showed that the particles were still of colloidal size, and a nitrogen surface area run on some dry powder recovered by this technique indicated that the mean particle diameter was about 30 millimicrons.

This copper powder was used to prepare a copper-aluminum alloy which had the composition of the commercial alloy known as 24S alloy. This alloy has 4.5 parts of copper, 1.5 parts of magnesium, .6 part of manganese, and 93.4 parts of aluminum. The experimental alloy was of identical composition, except for the alumina contained inside the copper powder.

The metal components of this alloy were melted and brought to a temperature of 815° C and maintained in the molten state for a period of thirty minutes. The mixture was then air-quenched and extruded into rods approximately one-fourth inch in diameter, from an initial size of one inch diameter. This extrusion was accomplished at a temperature of about 450° C. The alloy was then given a solution heat treatment in the temperature range of from 488° to 499° C for a period of three hours. It was then

quenched in cold water and precipitation-hardened at room temperature over a period of three days. This cycle of heat treatment corresponds to the so-called T-4 condition.

5 The tensile strength of this alloy was tested at a temperature of 600° F and was shown to be 24,000 psi. A commercial alloy of the same composition but containing no alumina has a tensile strength of about 7,000 psi at  
10 this temperature. This example shows the considerable improvement in tensile strength which can be brought about by the inclusion of only 0.7 volume per cent of a colloidal alumina in an aluminum-copper alloy.

15 The example illustrates the technique of forming a colloidal oxide dispersion in a high-melting metal and dissolving this high-melting metal in a lower-melting metal containing an active metal as a wetting agent. In  
20 this example, the active metals were magnesium, aluminum, and manganese, and the high-melting, inactive metal was copper.

#### EXAMPLE 25.

25 A procedure substantially identical with that of Example 26 was employed to introduce 0.6 volume per cent of colloidal alumina into an alloy comprising 90 parts of aluminum, 10 parts of copper, and 4 parts of magnesium.

30 The tensile strength of this alloy tested at 660° F was 7100 psi, and this compares with a tensile strength of 2,120 psi on an otherwise identical control alloy prepared in a similar manner except containing no  
35 colloidal alumina. This 300% improvement in the tensile strength of an alloy again illustrates the profound strengthening action of colloiddally dispersed refractory oxides on metals and alloys.

#### EXAMPLE 26.

40 This example illustrates the application of a process of the invention to the preparation of a novel, high-melting metal product containing a dispersed refractory oxide.

45 A masterbatch of molybdenum containing 3% by weight colloidal zirconia was prepared by precipitating molybdenum pentoxide around the surface of the colloidal zirconia particles by adding ammonium  
50 hydroxide to an aqueous solution of the molybdenum pentavalent chloride. This material was then dried and reduced under hydrogen for a period of ten hours at a temperature of 1000° C.

55 The product was dissolved in molten titanium at the melting point of titanium, in an arc furnace in which the sample was resting on water-cooled copper supports. The ratio of molybdenum to titanium used was  
60 30:70. This sample was remelted several times to insure complete homogenization of the alloy. The alloy was then rolled to break down the cast structure, and its high-temperature properties evaluated.

65 The product showed significant improve-

ment in high-temperature creep resistance over a control alloy of otherwise identical composition, but containing no colloidal zirconia.

#### EXAMPLE 27.

70 This example describes a niobium base alloy containing submicron-sized thoria particles. This alloy is typical of a preferred class of products of the invention, namely  
75 those containing upward of 50 weight per cent niobium. Such niobium base alloys can, in addition, contain up to 15% titanium, up to 20% of molybdenum, and up to 35% tungsten, the total of these additional  
80 elements being less than 50%. More specifically, the process of this example can be used to prepare such alloys at 64 Nb-10 Ti-6 Mo-20 W, 57 Nb-10 Ti-3 Mo-30 W, 60 Nb-10 Ti-30 W. Other niobium base  
85 alloys may be prepared containing zirconium, for example, 80 Nb-5 Zr-15 W and 85 Nb-5 Zr-10 Mo.

In the preparation of the melted and cast composition of this example, the thoria was added to the alloy via a molybdenum-thoria masterbatch. It will be understood that a  
90 tungsten-metal oxide masterbatch can be used in addition to or in place of a molybdenum-metal oxide masterbatch in preparing alloys containing tungsten.

95 The thoria sol used to prepare the masterbatch was made by dispersing calcined thorium oxalate,  $\text{Th}(\text{C}_2\text{O}_4)_2$ , in water containing a trace of nitric acid, the thorium oxalate having been precipitated from  
100 thorium nitrate. The precipitate was washed, dried at 650° C for two hours, slurried in 6 N  $\text{HNO}_3$  for two hours, centrifuged, the precipitate reslurried in water, recentrifuged and finally slurried in water with sufficient  
105 anion-exchange resin in the hydroxyl form to raise the pH to 3.5. The resulting product was a thoria sol containing 25 millimicron, discrete thoria particles.

110 This thoria colloidal product was next embedded in a matrix of molybdenum hydroxide. The reactor used to accomplish this consisted of an acid-resistant steel tank with a conical bottom. The bottom of the  
115 tank was attached to acid - resisting piping, to which were attached three inlet pipes through T's. The piping was attached to a circulating pump, and from the pump the line was returned to the tank. Initially, the  
120 tank was charged with 5 liters of water. The atmosphere in the tank was nitrogen.

125 Through the first T, 5 liters of  $\text{MoCl}_5$  solution (2732 grams  $\text{MoCl}_5$  containing the equivalent of 960 grams Mo Metal) was added; through the second, 5 liters of 15 molar  $\text{NH}_4\text{OH}$  solution; and through the third, 5 liters of  $\text{ThO}_2$  sol containing 70.9 grams  $\text{ThO}_2$ . The particles in the  $\text{ThO}_2$  sol were 25 millimicrons in diameter, dense and discrete.

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The solutions were added to the reactor simultaneously. The rate of addition was held constant and uniform over the forty-five-minute period required for total addition.

- 5 The pH of the slurry at the end of the reaction was 8.7. A nitrogen atmosphere was maintained over the slurry during the reaction.

- 10 By adding equal volumes of  $\text{MoCl}_3$  solution,  $\text{NH}_4\text{OH}$  solution and  $\text{ThO}_2$  sol during any given time interval of the reaction, the ratio of  $\text{ThO}_2$  to  $\text{MoO}(\text{OH})_3$  in each fraction of precipitate was held constant.

- 15 The precipitate was recovered by filtration under a blanket of nitrogen gas. It was a brown, gelatinous mass of  $\text{MoO}(\text{OH})_3$  with 25 millimicron  $\text{ThO}_2$  particles embedded uniformly throughout it.

- 20 The precipitate was dried at  $240^\circ\text{C}$  overnight, micropulverised to 100 mesh and finally heated at  $450^\circ\text{C}$  for two hours to remove the last traces of chloride.

- 25 The resulting black powder was placed in a furnace. The temperature in the furnace was slowly raised to  $600^\circ\text{C}$ , while a steady stream of purified hydrogen and argon was passed over the powder. Next the temperature was raised to  $950^\circ\text{C}$  for sixteen hours and finally to  $1300^\circ\text{C}$  for eight hours. During  
30 the latter stages of reduction, purified hydrogen gas was passed over the Mo-Tho<sub>2</sub> powder.

- 35 The resulting product was a powder consisting of molybdenum metal particles having 100 millimicron thoria particles dispersed throughout. The particles of powder were -100 and +200 mesh.

- 40 The nature of the thoria particles in the powder was determined by dissolving the metal in a mixture of nitric and hydrochloric acids, and recovering the colloidal  $\text{ThO}_2$  by centrifuging, washing with dilute  $\text{NH}_4\text{OH}$ , and with  $\text{H}_2\text{O}$ , and finally peptizing with dilute  $\text{HNO}_3$ . The thoria particles appeared  
45 discrete, spherical, and 100 millimicrons in size when viewed at 25,000 magnification with an electron microscope.

- 50 The product analyzed as follows: 91.5% molybdenum by weight, 7.63% thoria (or 7.85%  $\text{ThO}_2$  by volume), and 1.30% total oxygen, or only 0.37% oxygen in excess of that in the refractory oxide.

- 55 Using the molybdenum-thoria masterbatch prepared as above, a niobium base alloy was made, using the following casting technique.

- 60 A granular mixture of 80% by weight niobium (99.7% pure), 10% by weight titanium (99.5% pure), and 10% by weight of molybdenum-thoria (prepared as above indicated) was non-consumably arc-melted on a water-cooled copper hearth in a clean argon atmosphere. The as-cast button of filled alloy thus prepared was forged at  $1100^\circ\text{C}$  to about 50% reduction in thickness; pieces  
65 of the forged alloy were then heat treated

for nine hours at  $2000^\circ\text{C}$  in vacuum and rapidly cooled to room temperature. During the heat treatment at  $2000^\circ\text{C}$ , the grain size of the alloy reached a magnitude described by approximately ASTM Grain Size No. 4. An alloy of similar composition but containing no  $\text{ThO}_2$  exhibited a grain size greater than ASTM No. —3 after similar processing. Therefore, the presence of  $\text{ThO}_2$  as introduced by the present technique caused considerable restraint of grain growth during exposure of the alloy at high temperature.

Another portion of the alloy, after forging to a 50% reduction in thickness, was heated for one hour at  $1100^\circ\text{C}$ , a treatment sufficient to cause recrystallization of an alloy of the same composition but containing no refractory oxide particles. No metallographic evidence of recrystallization was seen in the alloy containing refractory oxide particles. Upon heating of a forged sample for six hours at  $1100^\circ\text{C}$ , partial recrystallization occurred. Therefore, the presence of refractory oxide particles retarded recrystallization of a cold-worked alloy.

Still another portion of the alloy, after forging, was heat treated nine hours at  $2000^\circ\text{C}$ , cooled to room temperature, reheated to  $1200^\circ\text{C}$  and held at  $1200^\circ\text{C}$  for twelve hours, cooled to room temperature and machined into specimens suitable for hot hardness testing. Diamond pyramid hardness numbers (DPHN) so obtained were as follows: (a) at  $900^\circ\text{C}$ , DPHN was 220, (b)  $1000^\circ\text{C}$  was 190, (c)  $1100^\circ\text{C}$  was 145, (d)  $1200^\circ\text{C}$  was 90, (e)  $1300^\circ\text{C}$  was 56, and (f)  $1400^\circ\text{C}$  was 40. In general the hardness numbers were at least twice as high as those for a control alloy containing no thoria.

In preparing compositions of the type above described, care must be exercised in the melting process. For example, if the arc is focused on the molybdenum-thoria masterbatch for prolonged periods, the thoria may slag and melt. In order to avoid this, the metal powders are thoroughly mixed prior to melting. In another approach, the molybdenum-thoria is added to molten titanium. In such systems, wetting appears to be more rapid, thus protecting the thoria from prolonged, direct exposure to the arc. A molybdenum-thoria-titanium composition is then added to molten niobium along with other alloying constituents to prepare the desired final composition.

#### EXAMPLE 28.

This example is similar to Example 4, except that a molybdenum-7% zirconia masterbatch was used in place of molybdenum-thoria. After heat treatment, this product showed a grain size of approximately ASTM No. 0. Therefore, the presence of the  $\text{ZrO}_2$  caused restraint of grain growth during

exposure of the alloy at high temperature.

A portion of the forged alloy was heat treated and hot hardness tested. Hardness data were: DPHN at 1000° C of 190, at 1100° C of 175, at 1200° of 120, at 1300° C of 70 and at 1400° C of 45.

#### EXAMPLE 29.

Titanium base alloys of the type Ti—2—30 Mo—0—10 Al can also be made by the process of this invention. Other constituents such as chromium, vanadium, and tungsten can also be present up to 15%. For example: 15 grams of a molybdenum-20% thoria masterbatch was powder blended with 264 grams of high-purity titanium powder. This mixture was arc-melted along with 21 grams of pure aluminum to form an alloy consisting of Ti—7 Al—4 Mo—1 ThO<sub>2</sub>. The thoria remained small and well dispersed throughout the alloy and did not slag.

#### WHAT WE CLAIM IS:—

1. A process for producing a cast metalliferous composition having a melting point above 50° C which comprises dispersing in a molten mass of the metal, submicron-sized particles of at least one metal-wettable refractory metal oxide insoluble therein, said particles having a surface area, in square meters per gram, of from 12/D to 1200/D when the mixture has a melting point of 50 to 720° C and from 6/D to 1200/D when the said melting point is above 720° C where D is the density of the wettable refractory in grams per milliliter, there being present in the mixture at least the minimum proportion of an active metal which prevents drossing out of the refractory particles when the molten mixture is maintained in a quiescent state for  $\frac{1}{2}$  hour and, when the melting point of the mixture is above 720° C, at least 4 mol per cent, based on the refractory particles, the active metal being one having an oxide irreducible by hydrogen below 1000° C and having a free energy of formation at 27° C. above 88 kcal. per gram atom of oxygen, and thereafter casting the molten mixture.

2. A process for producing a metalliferous composition, which comprises dispersing in a molten mass of a metal having a melting point of from 50° C. to 720° C., submicron-sized particles of at least one metal-wettable refractory metal oxide insoluble therein having a surface area, in square meters per gram, of from 12/D to 1200/D, where D is the density of the wettable refractory in grams per milliliter, there being present in the mixture at least the minimum proportion of an active metal which prevents drossing out of the refractory particles when the molten mixture is maintained in a quiescent state for  $\frac{1}{2}$  hour, the active metal being one having an oxide irreducible by hydrogen below 1000° C. and having a free energy

of formation at 27° C. above 88 kilocalories per gram atom of oxygen, and thereafter solidifying the dispersion.

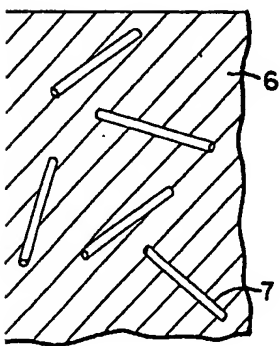
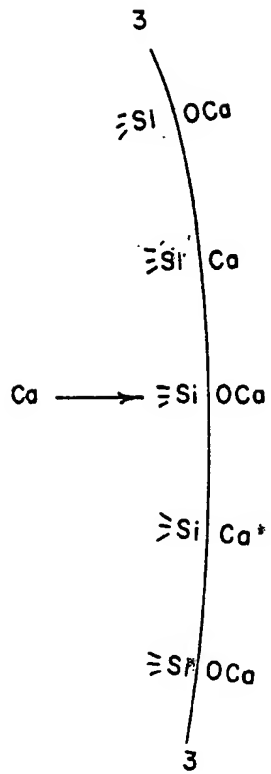
3. A process according to claim 2 in which the refractory metal oxide is added to the molten metallic mass in contact with from  $7.5 \times 10^{-4}$  A to  $7.5 \times 10^{-2}$  A grams of oxygen per gram of the refractory metal oxide, A being the surface area of said refractory metal oxide in square meters per gram.

4. A process for producing a metalliferous composition having a melting point above 720° C., the steps comprising mixing a dispersion of refractory metal oxide particles in an inactive metal with a molten mass of metal, said particles being substantially discrete, being insoluble in the metal mixture, having an average dimension of 5 to 1000 millimicrons, and having a surface area, in square meters per gram, of from 6/D to 1200/D, where D is the density of the refractory in grams per milliliter, there being present in the molten mass at least 4 mol per cent, based on the oxide particles, of an active metal, the intensity of mixing being sufficient to maintain dispersion of the oxide particles in a substantially discrete state in the mixture and the active metal being one having an oxide irreducible by hydrogen below 1000° C. and a free energy of formation at 27° C. above 88 kcal. per gram atom of oxygen, and thereafter casting the molten mixture.

5. A process according to claim 4, in which the refractory oxide has a free energy of formation at 1000° C. greater than 90 kcal. per gram atom of oxygen.

6. A cast metalliferous composition having a melting point above 50° C., said composition comprising a dispersion in a mixture of (a) a metal which has a melting point above 50° C, and has an oxide that is reducible by hydrogen below 1000° C. and has a free energy of formation ( $\Delta F$ ) at 27° C below 88 kcal. per gram atom of oxygen when the composition is one having a melting point above 720° C., with (b) an active metal having an oxide which is irreducible by hydrogen below 1000° C. and has a free energy of formation at 27° C. above 88 kcal. per gram atom of oxygen and (c) substantially discrete particles, having an average dimension of 5 to 1000 millimicrons and a surface area, in square meters per gram, of 12/D to 1200/D when the composition has a melting point of 50 to 720° C. and from 6/D to 1200/D when the said melting point is above 720° C. where D is the density of the refractory in grams per milliliter, said particles being at least one refractory metal oxide which is insoluble in said metal mixture, is thermally stable at the melting point of the composition, has a melting point above that of the composition, and has a  $\Delta F$  at 1000° C. above the  $\Delta F$

- of the oxide of the active metal and above 60 kcal. for compositions having a melting point from 50 to 720° C. and above 90 kcal. for compositions having a melting point above 720° C. the proportion of active metal being at least the minimum proportion which prevents dropping out of the refractory particles when the composition is melted and maintained in a molten, quiescent state for  $\frac{1}{2}$  hour, and for compositions melting above 720° C. said proportion being at least 4 mol per cent, based upon the refractory particles.
7. A cast, metalliferous composition having a melting point in the range of 50 to 720° C. said composition comprising an active metal having an oxide which is irreducible by hydrogen below 1000° C and has a free energy of formation at 27° C above 88 kcal. per gram atom of oxygen, said metal having dispersed therein up to 80 per cent by volume of refractory oxide having a melting point above 1000° C., and a free energy of formation at 1000° C. above 60, the refractory oxide being in the form of substantially discrete particles having an average dimension of 5 to 500 millimicrons and a surface area, in square meters per gram, of  $12/D$  to  $1200/D$  where D is the density of the particles in grams per milliliter.
8. A composition according to claim 7, wherein the active metal is magnesium, aluminium, zinc, lithium, sodium, potassium, rubidium, cesium, calcium, barium, or strontium, or an alloy of two or more of these metals.
9. A composition according to claim 7 or 8, which also comprises a metal having a melting point above 50° C. and having an oxide reducible by hydrogen below 1000° C.
10. A cast metalliferous composition having a melting point above 720° C., said composition comprising a dispersion, in a mixture of (a) a metal having a melting point above 50° C., and having an oxide reducible by hydrogen below 1000° C. and a free energy of formation at 27° C. below 88 kcal. per gram atom of oxygen, with (b) an active metal having an oxide irreducible by hydrogen below 1000° C. and a free energy of formation at 27° C. above 88 kcal. per gram atom of oxygen, of (c) substantially discrete particles, having an average dimension of 5 to 1000 millimicrons and a surface area, in square meters per gram, of  $6/D$  to  $1200/D$  where D is the density of the particles in grams per milliliter, of at least one refractory metal oxide which is insoluble in said metal mixture, is thermally stable at the melting point of the composition, and has a melting point above that of the composition and a free energy of formation ( $\Delta F$ ) at 1000° C. above 90 kcal. per gram atom of oxygen and above the  $\Delta F$  of the oxide of the active metal, the proportion of active metal being at least 4 mol per cent based upon the dispersed refractory oxide particles.
11. A composition according to claim 10, in which the refractory oxide has a free energy of formation greater than 105 kcal. per gram atom of oxygen.
12. A composition according to claim 10 or 11, in which the refractory oxide has an average particle size of 5 to 500 millimicrons.
13. A composition according to any of claims 10 to 12, in which the proportion of refractory oxide is up to 10% by volume.
14. A composition according to any of claims 10 to 13, in which the active metal is one having a melting point above 1200° C.
15. A composition according to claim 14 in which the active metal is titanium, the proportion of titanium being at least 50% by weight.
16. A composition according to claim 14, in which the active metal is niobium, the proportion of niobium being at least 50% by weight.
17. A niobium base alloy according to claim 16, containing from 2 to 20% by weight of molybdenum.
18. A niobium base alloy according to claim 16 containing from 2 to 35% of tungsten.
19. A niobium base alloy according to claim 16 in which the refractory oxide is thoria.
20. A process according to any of claims 1 to 5 for producing a metalliferous composition substantially as herein described with reference to any of the Examples.
21. The metalliferous compositions hereinbefore specifically described.
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Chartered Patent Agents,  
Northumberland House,  
303/306, High Holborn,  
London, W.C.1.  
For the Applicants.



G. 3

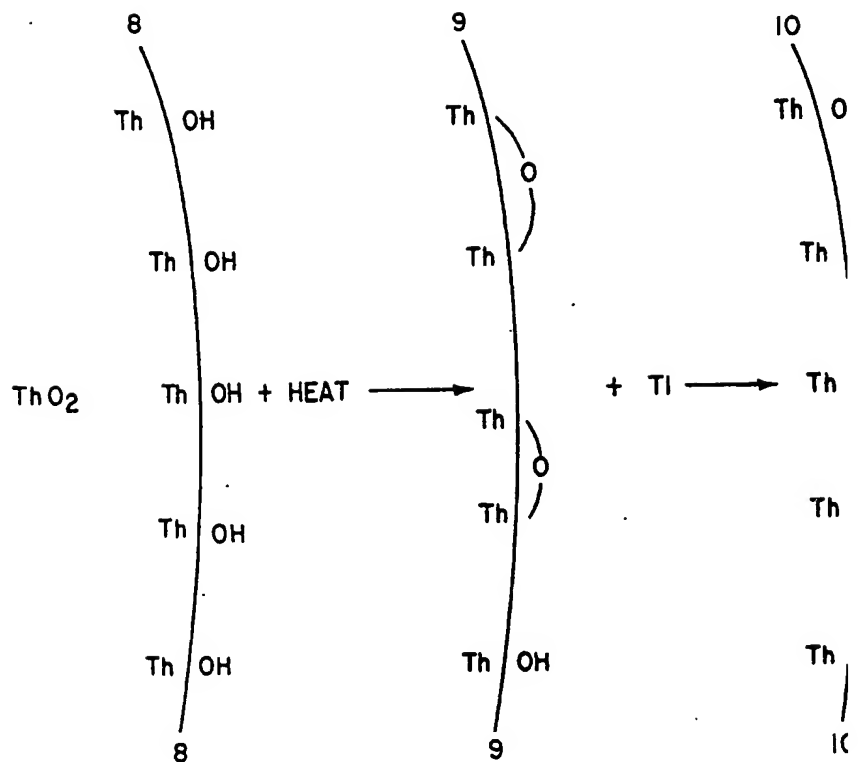


FIG. 4

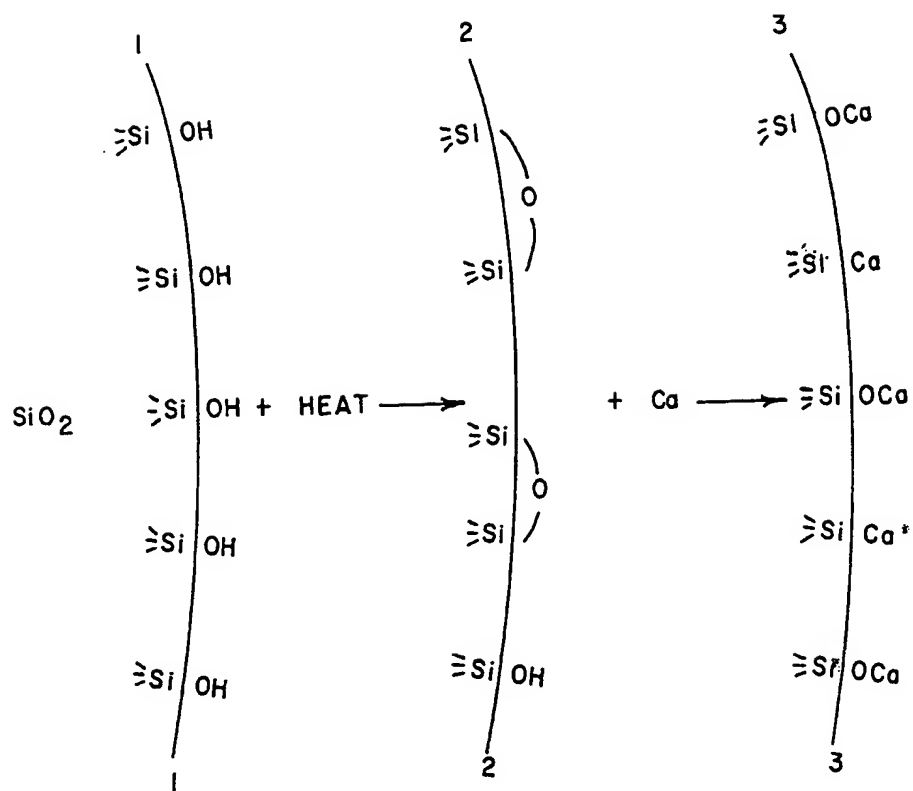


FIG. 1

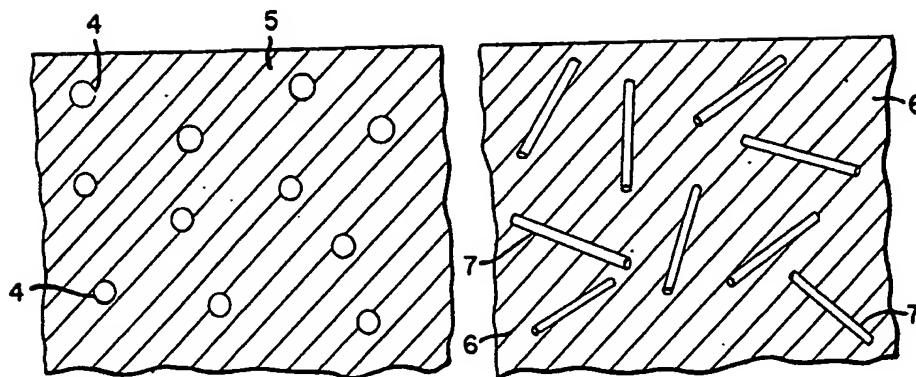


FIG. 2

FIG. 3

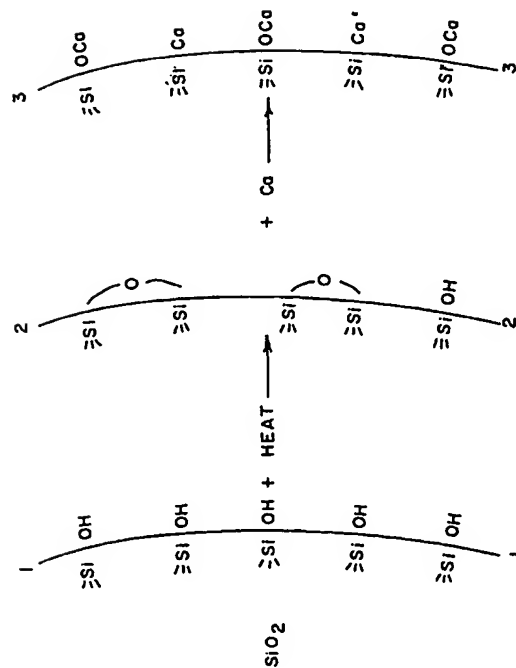


FIG. 1

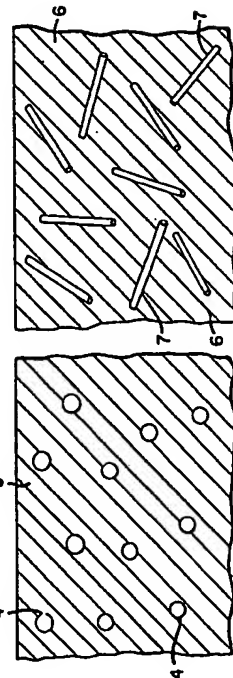


FIG. 2

FIG. 3

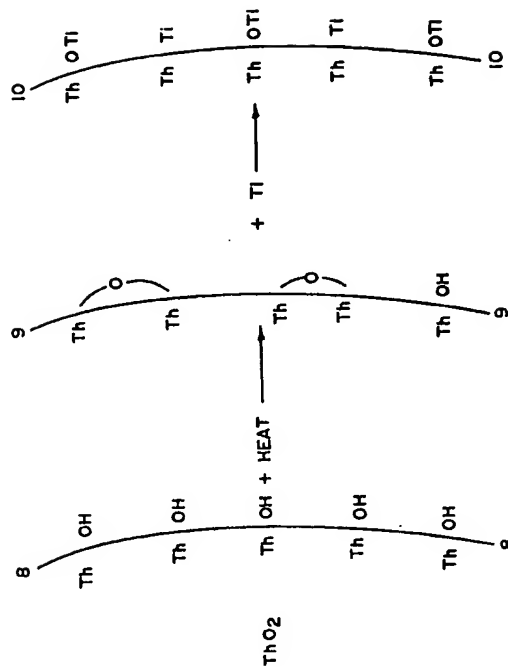


FIG. 4